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DETERMINATION OF IGNITION POINTS OF LIQUID FUELS
UNDER PRESSURE.

By J. Tausz and F. Schulte.

From "Zeitschrift des Vereines Deutscher Ingenieure,"
May 31, 1924.

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TECHNICAL MEMORANDUM NO. 299.

DETERMINATION OF IGNITION POINTS OF LIQUID FUELS
UNDER PRESSURE.*

By J. Tausz and F. Schulte.

Two series of experiments were tried, in order to determine the ignition point at any desired pressure, the first series at constant and the second at varying pressure. The results differ greatly and indicate that testing under pressure, in the investigation of liquid fuels, can be done best in the laboratory and that the determination of the ignition points in an open vessel furnishes no certain indication of the behavior of the fuel in the engine since, contrary to the general impression, the ignition points of the various fuels are very differently affected by changes in pressure; hence the differences in the corresponding calculations of the temperature and final compression required in a Diesel engine.

General remarks on ignition-point determinations.— In recent years the determination of the ignition points has become more general as a means of judging liquid fuels. From the results of such determinations it is usually possible to judge the suitability of the various fuels for the Diesel engine. The determination at ordinary atmospheric pressure, i.e., in an open vessel, furnishes,

* From "Zeitschrift des Vereines Deutscher Ingenieure," May 31, 1924, pp. 574-578.

however, only a general basis, since changes in pressure cause very different changes in the ignition points.

The assumption of Wollers and Ehmke, as likewise of Alt (see N.A.C.A. Technical Memorandum No. 281), that the absolute ignition temperatures of different liquid fuels continue to bear the same relation to one another at different pressures, is not correct. On the contrary, the ignition points, even of successive fractions of the same oil, often vary quite differently with changing pressure. The differences are still greater for different oils.

The inadequacy of the determination of the ignition point in an open vessel is demonstrated by the fact that a coal-tar oil, whose ignition point in an open vessel was considerably lowered by the addition of 10% of easily ignited shale oil, showed a higher ignition point at a high pressure than the pure coal-tar oil and also by the fact that the ignition point, which is generally lowered by pressure can, in many instances, be raised by pressure up to a certain degree.

As determined in an open vessel, the ignition point is a definite physicochemical property. Divergences in the results obtained by different investigators are partly due to the fact that substances called by the same name, like gasoline, differ considerably in their composition, according to the source of the petroleum from which they are obtained, and partly to the fact that slight impurities, which may greatly affect the ignition point at normal pressure, are disregarded. For example, chemically pure benzene (free

from sulfur compounds) first ignites at 662°C (1224°F), while benzene containing sulfur (also commonly called pure) ignites at 577°C (1071°F). Since this difference in composition was disregarded, benzene has hitherto been assigned a much too low ignition point.

Variations in the ignition point of a substance are also often ascribable to deficiencies in the experimental apparatus. If the essential conditions for accurate determinations (such as the exclusion of catalytic influences, uniform temperature in the vessel, correct proportions of fuel and air or oxygen) are fulfilled, the results, even for greatly differing apparatus, are identical and always reobtainable.

In order to obtain the important uniform distribution of heat, the ignition vessel must be enclosed in an oven lined with asbestos, so that, after the flame is removed, the temperature of the vessel will fall but $2\text{--}3^{\circ}\text{C}$ ($3.6\text{--}5.4^{\circ}\text{F}$) per minute. Moreover, greater accuracy can be obtained by taking the ignition point while the temperature is falling than while it is rising, as has been customary. The temperature is first raised 50°C (90°F) at a time, until ignition takes place. It is then allowed to cool and the exact ignition point is determined during the cooling.

The capacity of many ignition-point testers is so small that unreliable results are obtained, especially in the determination with air, on account of the impossibility of obtaining the right proportions of fuel and air. Good results were obtained with an ignition-point tester having a capacity of 25 cm^3 (1.52 cu.in.),

through which 200-300 cm³ (12.2-18.3 cu.in.) of air or 70-80 cm³ (4.27-4.88 cu.in.) of oxygen was conducted per minute, with the addition of a 15-30 mg (0.23145-0.4629 grain) drop of fuel, such as falls from a finely pointed pipette.

At a temperature 30 to 50°C (54-90°F) above the ignition point the fuel generally ignites immediately, i.e., within 0.02-0.05 second after the introduction of the fuel. This interval is longer when the temperature is falling. The delay in the ignition at the minimum temperature at which it can take place (i.e., at the ignition point) varies greatly and may amount to as much as 5 seconds. As Hawkes found in his experiments ("Engineering," 1920, Vol. 110, p.749), the delay is about the same for ignition under pressure.

Ignition depends on the chemical composition of the fuel and the preceding chemical changes, which differ for different pressures and temperatures. Physical conditions, such as the fineness of division and diffusion, have no immediate effect on the ignition temperature, but affect only the completeness and rapidity of the combustion (Compare Wartenberg, "Zeitschrift des Vereines Deutscher Ingenieure," 1924, Vol. 68, p.153, and Haber and Wolf, "Zeitschrift für Angewandte Chemie," 1923, Vol. 36, p.373).

The chemical changes preceding ignition are very complex and very difficult to investigate, on account of their rapidity. The inadequacy of former hypotheses is demonstrated by several conspicuous phenomena, which they fail to explain. For example, the ignition temperature in oxygen is not always lower than in air, but

many substances have a higher ignition temperature in oxygen than in the air. Furthermore, the ignition point in oxygen is not always the same as in air under a pressure of 5 atmospheres, in which the amount of oxygen is the same as in the same volume of pure oxygen at normal pressure. The ignition points differ greatly in these two cases and the discrepancy increases with the size of the molecules and the quantity of unsaturated compounds contained in the fuel. Moreover, the sensitiveness of many substances is so great that even variations in the barometer considerably affect the ignition point and many substances (e.g., anhydrous butyric and valeric acids) even have two ignition points in air. The former first ignites in air at 320°C (608°F) with a delay of 2 to 3 seconds. Above 322°C (611.6°F) no real ignition occurs, but only quiet combustion. Only above 350°C (662°F) does real ignition again take place, with a delay of about 1 second.

According to Tausz, these and other phenomena can be explained by the creation of primary substances (peroxides) which, although the time is so short that no extensive decomposition or complete evaporation of the fuel can occur before the ignition, still plays an important role, since, even in very small quantities, they exert a strong influence by their sudden disintegration.*

* The chemical changes before ignition, previous hypotheses and the new hypothesis resulting from our experiments are minutely described in "Mitteilungen des chem.-techn. Instituts der Techn. Hochschule, Karlsruhe," published by Knapp in Halle. The ignition points of the different substances both in an open vessel and under pressure, as also the various devices required for their determination, are also fully described.

Determination of ignition point under pressure.— As already mentioned, the determination of the ignition point in an open vessel furnishes no certain indication of the suitability of a liquid fuel for the Diesel engine, since the ignition points of different fuels vary differently with increasing pressure. It is of little use for testing unsuitable fuels (such as coal-tar oil) which are rendered utilizable by additions, since a lowering of the ignition point at normal pressure may, under high pressure in an engine, be converted into an elevation of the ignition point. Hence it was sought to execute the experiments under pressure and two different arrangements were tried. In experiments A the ignition was effected at constant pressure without spraying. In experiments B the fuel was sprayed by compressed air, so that the changes preceding ignition took place under rapidly increasing pressure, the same as in a Diesel engine.

Experiments A (without spraying).— Fig. 1 shows the arrangement of the ignition-point tester. The introduction tube c is hermetically attached to the ignition block a by means of the screw-cap b. This tube can be closed at the top by means of the cap d. The pipe f leads to the manometer h and to the expansion valve i. The air intake valve is located in the pipe e. Near the top of the tube c, a packing box k is introduced, through which passes a rod with a wire loop m. The ignition block has, just below the ignition chamber, a hole for introducing the thermo-electric couple. The bottom of the ignition block is

protected from the gas flame by an asbestos disk. The introduction tube c is surrounded by a cooling jacket l. In order to effect a slow cooling, the ignition block is protected by an asbestos-lined sheet iron cylinder.

The fuel to be tested is enclosed in a glass bulb of about 0.25 cm^3 (1.52 cu.in.) capacity. The capillary tip of the bulb must not be fused together, since that might cause the experiment to fail, by the failure of the bulb to break.

The ignition block is brought to a certain temperature, the introduction tube begins to cool and the glass bulb is laid on the wire loop m. After the introduction tube is closed, it is filled with air under the desired pressure with the aid of the valve g. After the latter is closed and while the temperature of the ignition block is falling, the glass bulb is dropped into the ignition chamber by rotating the wire loop. If ignition occurs, which is indicated by the deflection of the manometer pointer, the cap d is removed and the interior cleared out with a strong current of air. The experiments are then continued at the same pressure and somewhat lower temperatures until the lowest temperature is found at which ignition occurs. Gasoline, benzene, petroleum, paraffin, lignite oil, shale oil and coal-tar oil were tested in the above manner.

As shown by Fig. 2, the ignition-point curves for pure aliphatic fuels are very similar and approach 200°C (392°F) at 12 atm. pressure. Shale oil ignites at a somewhat higher temperature, coal-tar oil considerably higher and benzene the highest of all.

Since the fuel was not sprayed and the pressure was constant in these experiments, the results cannot accurately indicate the behavior of the fuels in the Diesel engine. In order to approximate the conditions in the Diesel engine, the attempt was made to ignite the fuels in the finest possible spray. In the following experiments the pressure was so adjusted that the delay was eliminated and the ignition took place immediately after the fuel was injected.

Experiments B (with spraying).— The arrangement for this purpose is shown in Figs. 3-5. The introduction tube *b* and the ignition block *f* are screwed into the iron block *a*. The introduction tube *b* can be closed by means of a cap *d* and has a cooling-water jacket *e*. The compressed air is heated in the block *a* before entering the tube *b*. A spherical non-return valve *v* is inserted in the air-intake pipe, so that the burned gases cannot enter the container *m*. The block *a* has another connection leading to the manometer *l*. There is also a chimney *q* connected with an asbestos-lined chamber *r*, which has an opening for the burner *s* under the ignition block *f*.

The tank *m*, for the blast air, was made so large that the tension of the latter did not diminish more than 0.3 atm. while filling the ignition point tester. The pressure in this tank was indicated by the manometer *n*. Between this tank and the ignition-point tester there was an inlet valve *o*, which, after a slight turn, opened wide enough to fill the apparatus with compressed air almost instantly. This tank was replenished from the compressed-air tank *p*.

In order to measure the temperature for the calibration of the thermoelectric couple, the nozzle h was first unscrewed from the air pipe and (after heating the ignition-point tester) the heat was shut off and the chimney valve t was closed. The temperature then fell at the rate of about 3°C (5.4°F) per minute. The temperature fall was measured by a thermometer reaching through the air pipe to the bottom of the ignition chamber and the readings of the millivoltmeter were simultaneously recorded. Since the upper portion of the mercury column had the temperature of the air pipe and hence of the cooling-water, around $12\text{--}15^{\circ}\text{C}$ ($54\text{--}59^{\circ}\text{F}$), a corresponding correction of the thermometer readings had to be made for the calibration.

After the readings had all been made, the temperature in the upper third of the ignition chamber was found, at the above-mentioned rate of cooling of 3°C (5.4°F) per minute, to be only $2\text{--}3^{\circ}\text{C}$ ($3.6\text{--}5.4^{\circ}\text{F}$) less than the temperature at the bottom of the chamber, near the thermoelectric couple. When the cooling was more rapid, this temperature difference attained 10°C (18°F).

In order to determine whether the preliminary heating of the compressed blast-air was sufficient, the following procedure was adopted. The apparatus was heated to about 500°C (932°F), the heat turned off and the chimney closed. While the air pipe was cooling, a thermometer was introduced as far as the mouth of the by-pass pipe j. The mercury bulb was protected with asbestos as far as the side turned toward the by-pass pipe, so that the mercury was not

cooled by the walls of the air pipe. Then a moderately strong air stream was blown through the iron block and the by-pass pipe into the air pipe and the temperature of the ignition block and of the inflowing air were taken simultaneously. At a temperature of 400°C (752°F) in the ignition block, the temperature of the inflowing air was $10\text{--}12^{\circ}\text{C}$ ($18\text{--}21.6^{\circ}\text{F}$) lower. At 200°C (392°F) in the ignition block, the differences were considerably greater, the temperature of the air being about 15°C (27°F) lower than in the ignition block. The preliminary heating was therefore quite sufficient.

If the ignition temperature of coal-tar oil is to be determined at 20 atmospheres, the intermediate tank is filled with air at 20.2 atm. from the compressed-air tank p, the ignition-point tester is heated to 450°C (842°F) and the air pipe b is simultaneously cooled by running water. The heating is then discontinued and the chimney closed. We then wait until the apparatus begins to cool slowly.

After the cap d is unscrewed, $1\text{--}3\text{ cm}^3$ ($0.061\text{--}0.183\text{ cu.in.}$) of coal-tar oil is dropped on the roll of wire gauze c by means of a pipette. The air pipe is then closed and the apparatus is filled, by a short turn of the valve o, with air at 20.2 atm.

The ignition is indicated by a short backward deflection of the pointer of the manometer l. The combustion gases are then released through the valve into the open air, the cap is removed and, after withdrawing the roll of wire gauze, the ignition chamber is blown out with a strong stream of air, in order to remove all traces of the combustion products.

The same process was repeated at 425°C (797°F) and ignition occurred. In the next trial at 400°C (752°F), there was no ignition. Several more trials, between 400 and 425°C , gave 418°C (784.4°F) as the final ignition point. The same fuel was tested in the same manner at other pressures.

The experiments were first performed without the nozzle h. The results varied so much, however, as to indicate the need of some change. In introducing the fuel without a nozzle, a considerable portion of it remained between the air pipe and the ignition chamber. After introducing the nozzle h, the discrepancies ceased and repetitions of the experiments gave the same results.

After a series of experiments, the ignition block and nozzle had to be unscrewed, so that the unburned carbon could be removed from the walls.

Results.— Taking into consideration the shortness of the time in which ignition must take place in a Diesel engine (less than 0.02 second in rapid engines), we cannot assume that the ignition is preceded by any considerable evaporation. Rather, in the most favorable case, only the outer layer of a drop evaporates and mingles with the air and ignites at the requisite temperature. The higher temperature, thus produced, then causes the ignition of all the rest of the fuel. In the vicinity of the ignition point, the temperature is generally too low to produce instantaneous ignition.

If coal-tar oil and shale oil are mixed in different proportions and then tested in Moore's ignition chamber at ordinary atmospheric

pressure, the ignition point falls continually as the proportion of shale oil is increased. Fig. 6 also shows the lack of agreement between experiments with air and with oxygen. In the experiments with oxygen, the ignition point fell, with increasing proportion of shale oil, at first very rapidly and then (above 40% of shale oil) much slower. In the experiments with air, the ignition point fell more uniformly. A mixture of equal parts of air and oxygen did not yield a mean ignition curve between the curve for air and the one for oxygen, but gave a curve hardly agreeing with either of the latter at any point and only slightly approaching the oxygen curve.

If the ignition points of these mixtures are determined under pressure and especially by the B method, they do not fall uniformly with increasing proportion of shale oil at a given pressure, but differ greatly from those obtained at 1 atmosphere. Fig. 7 gives the curves obtained by plotting the ignition temperatures against the pressures for pure shale oil and coal-tar oil and different mixtures of the same. With a mixture containing 10% of shale oil, the curve of the ignition points runs above that for coal-tar oil alone.

With 20% of shale oil the ignition curve intersects the curve for coal-tar oil at 8 atm. and runs, from there up, higher than the curve for the 10% mixture. Only mixtures containing above 30% of shale oil give ignition-point curves running consistently below the curve for pure coal-tar oil, even at the highest pressures. These differences can be better shown by a triaxial system of coordinates (Fig. 8), which gives the corresponding ignition-point curve for

each pressure.

Mixtures of coal-tar oil and lignite-tar oil (Figs. 9-10) exhibit similar phenomena though less pronounced. In these mixtures, more than 30% of lignite-tar oil (the more easily combustible substance) is required to lower the ignition points under pressure. When we employ a mixture of a more easily with a less easily combustible substance (e.g., anthracene oil) in a Diesel engine, we find that at least 50-60% of the former is required for good functioning.

The results of the B series of experiments agree with practical tests in an engine. With the help of this apparatus it is possible to determine, in the laboratory, the suitability of oils or mixtures for use in Diesel engines better than with the usual ignition-point testers. Fig. 11 is contrary to Alt's assumption that the temperature in a Diesel engine at the instant of ignition is about 100°C (180°F) higher than in an open ignition-point tester. According to Alt, the ignition point of benzene, which is 570°C (1058°F) in a current of oxygen in an open vessel, would be 720°C (1328°F) in a Diesel engine. Fig. 11 shows, however, that the ignition point of benzene lies between 450 and 500°C (842 and 932°F) at pressures of 20 to 40 atmospheres, such as exist in Diesel engines. Even in cases where, on account of delayed ignition, a somewhat higher temperature has to be assumed, the ignition point must still be far below 720°C (1328°F). Likewise, according to Fig. 11, the ignition temperature of gasoline in an engine, as given by Alt, is much too high.

These examples indicate that the computed ignition temperature in the engine is not correct. This value, as likewise the requisite final compression pressure, can hardly be computed, since the ignition temperatures of different fuels change very differently with increasing pressure.

Translation by Dwight M. Miner,
National Advisory Committee
for Aeronautics.

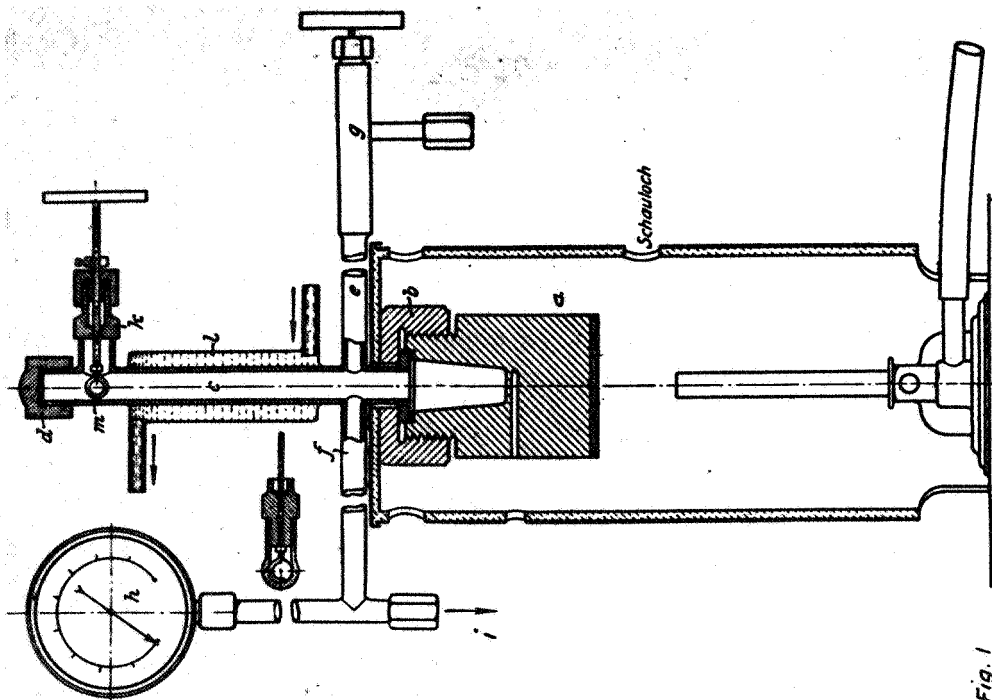
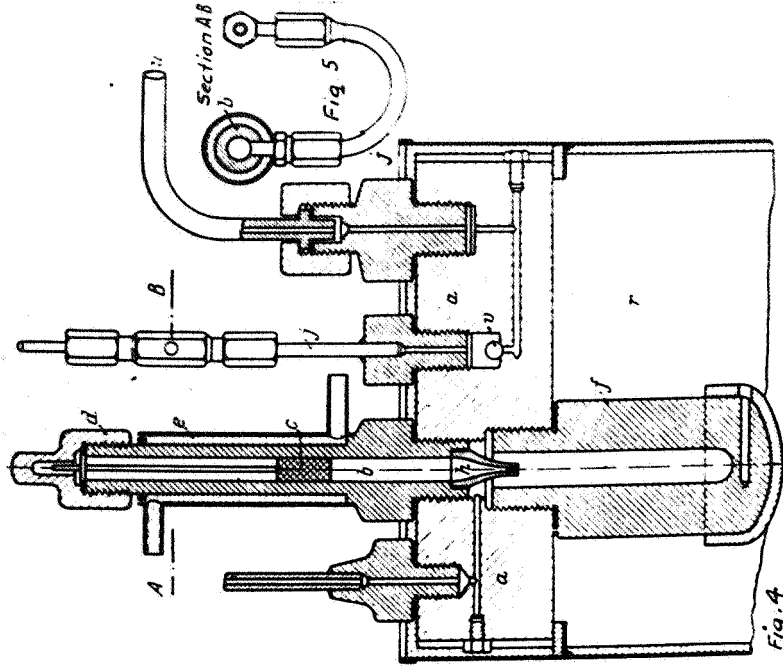


Fig. 1 Determination of ignition point under pressure. Arrangement A



Figs.4 & 5
Section through
ignition-
point
tester.

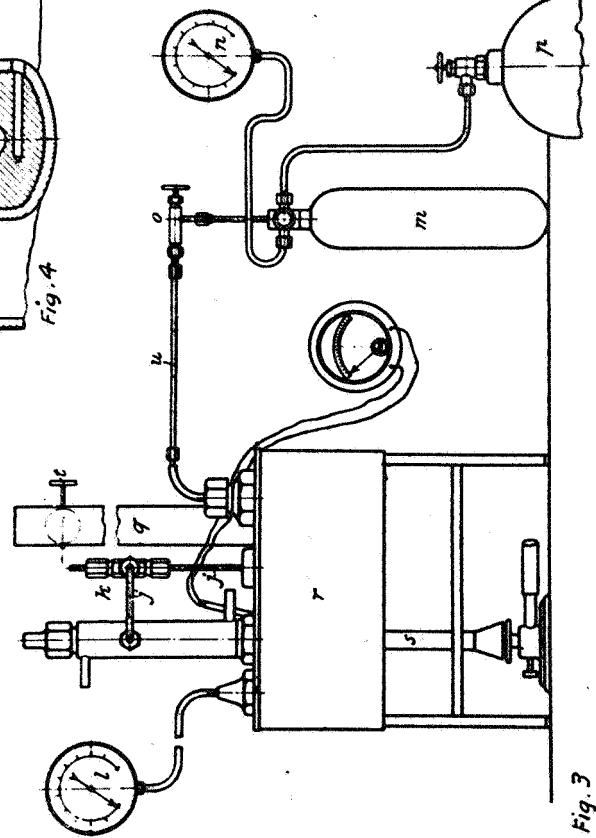


Fig. 3
Determination
of ignition
point under
pressure.
Arrangement B

Fig. 3

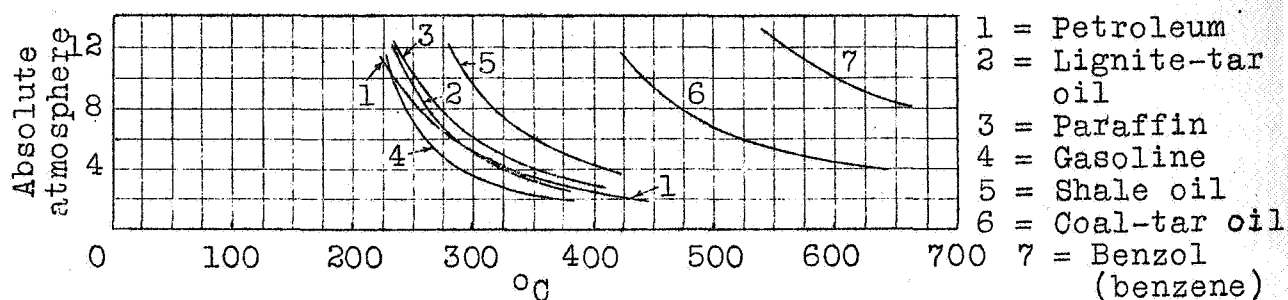


Fig. 2 Results of experiments A

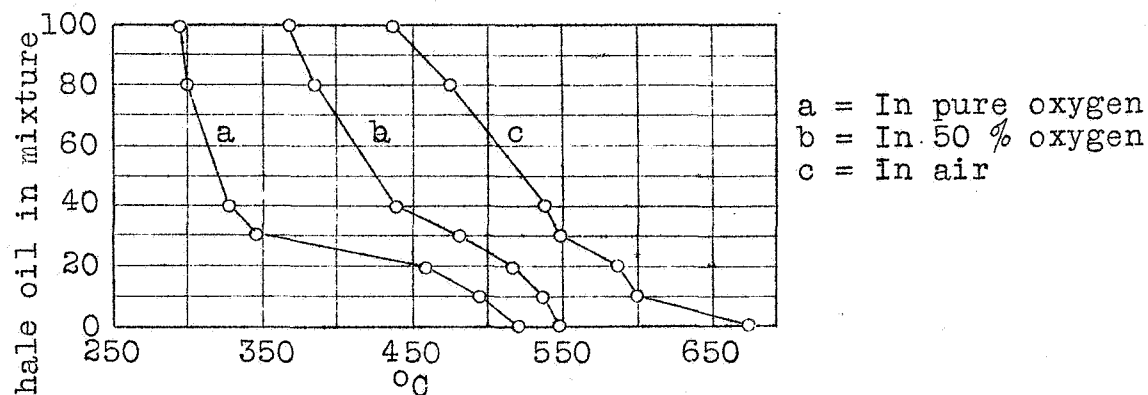


Fig. 6 Ignition points of mixtures of shale oil and coal-tar oil at 1 atm. in dry oxygen, in 50 % oxygen and in air.

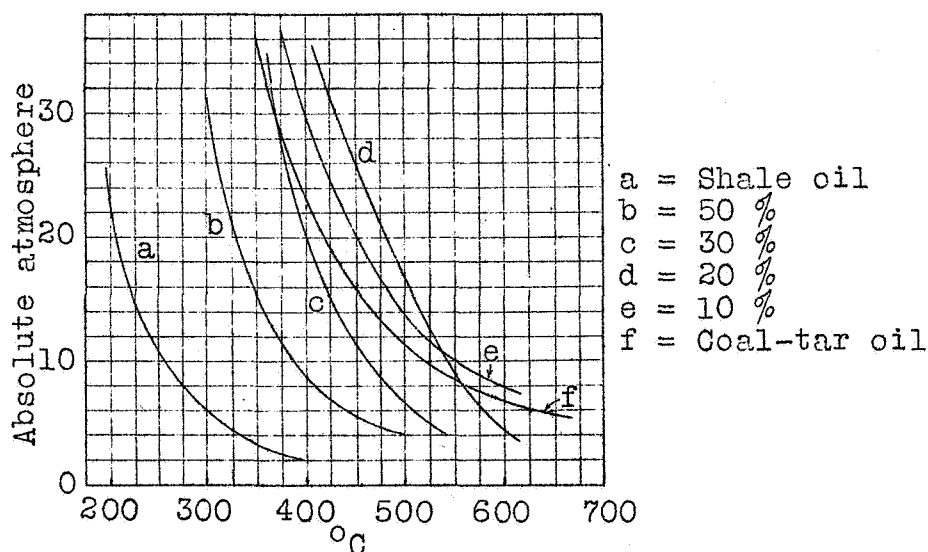


Fig. 7 Experiments B with coal-tar oil and shale oil and mixtures containing 10, 20, 30 and 50 % shale oil

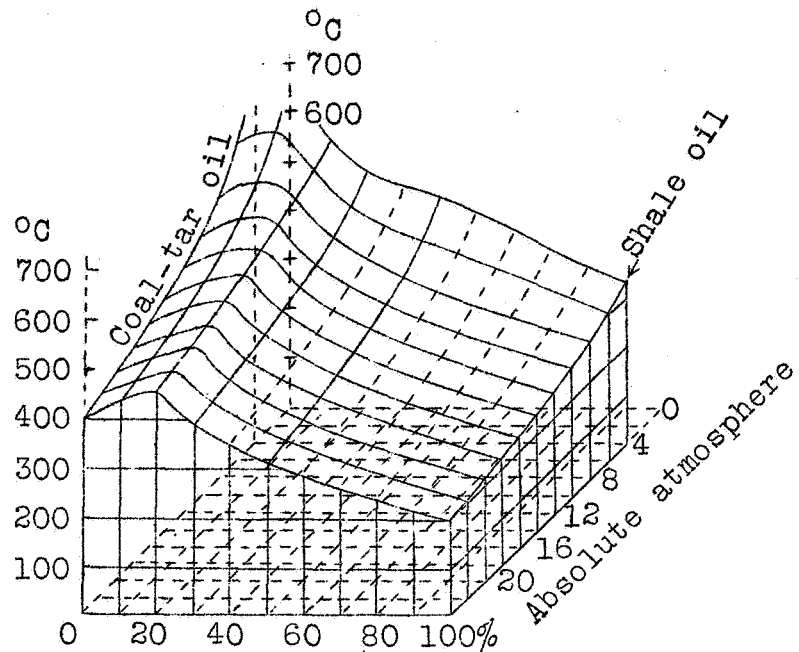


Fig.8 Ignition points of mixtures of shale oil and coal-tar oil.

E = Coal-tar oil
 A = Lignite-tar oil
 B = 50%
 C = 30%
 D = 10%

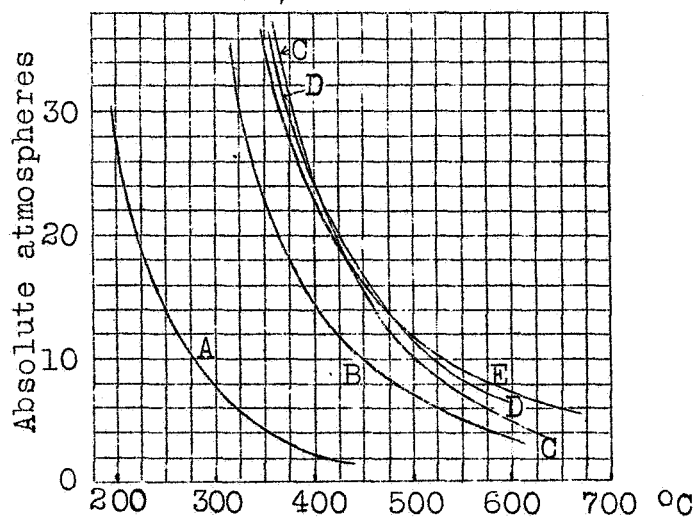


Fig.9 Ignition-point curves for pressure experiments with lignite-tar oil and coal-tar oil and mixtures containing 10, 30 and 50% lignite-tar oil.

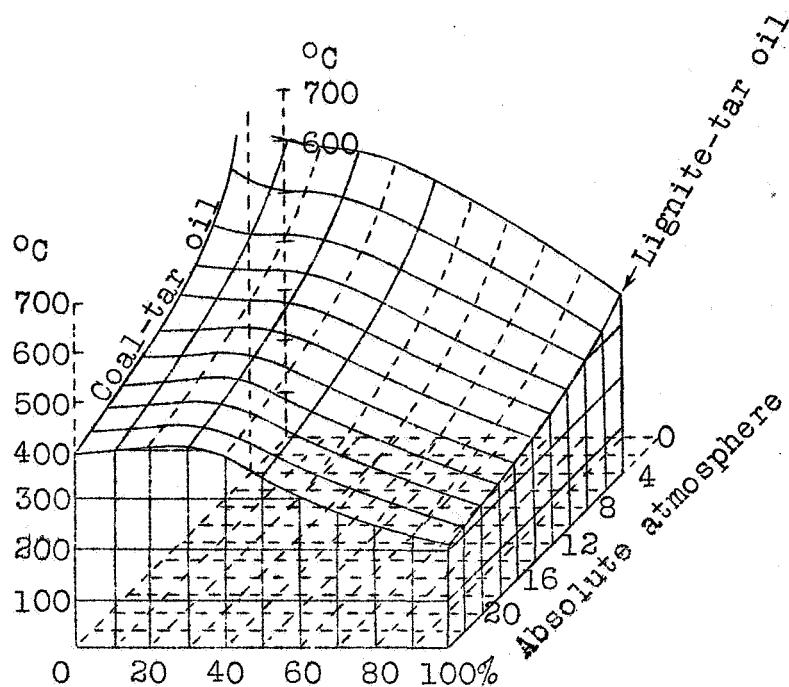


Fig.10 Ignition points of mixtures of lignite-tar oil with coal-tar oil.

- | | |
|---------------------|------------------|
| 1 = Paraffin | 5 = Gasoline |
| 2 = Petroleum | 6 = Cylinder oil |
| 3 = Gas-oil | 7 = Benzene |
| 4 = Lubricating oil | |

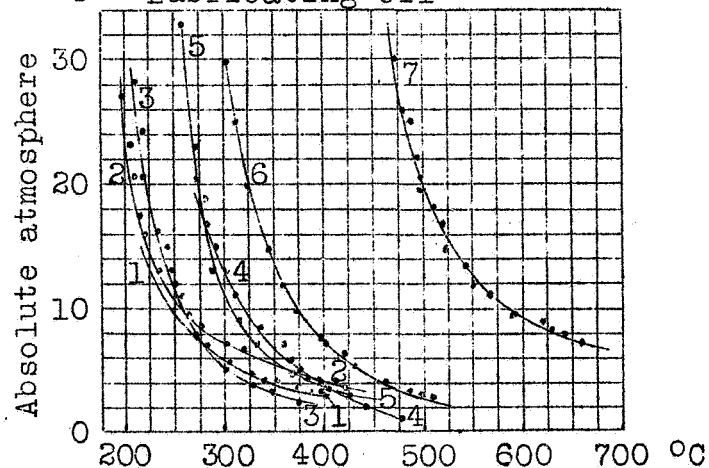


Fig.11 Results of pressure experiments B.